EXPERIMENTAL INVESTIGATION OF ULTRAHIGH VACUUM ADHESION AS RELATED TO THE LUNAR SURFACE

THIRTEENTH QUARTERLY PROGRESS REPORT
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J. A. Ryan
Principal Investigator
J. J. Grossman
Co-Principal Investigator
R&D/Space Sciences Department

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MISSILE & SPACE SYSTEMS DIVISION
DOUGLAS AIRCRAFT COMPANY
SANTA MONICA, CALIFORNIA

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ABSTRACT

Studies during this quarter have been concerned with (1) modifications of the experimental apparatus to permit study of the adhesional behavior of ultrahigh vacuum cleaved silicates in contact with metals of various surface state, and (2) construction of a second vacuum system to permit direct measurement of the magnitude and the distribution of electrostatic surface charging produced during cleavage. The modifications consist of installation of apparatus to permit argon ion sputtering and mechanical abrasion of the metal surfaces. The second vacuum system contains an adjustable electrometer probe with associated electronics and recording equipment.

The first run on silicate--metal adhesion has just begun and no data are available. Two runs measuring surface charge have been completed. They demonstrated that vacuum cleavage of silicates does indeed produce considerable surface charging, that this charging is macroscopically anisotropic, and that it persists over extended periods of time. Plots of charge magnitude versus time show a close correlation with previously obtained plots of adhesion force as a function of time.

1.0 INTRODUCTION

1.1 General

This report presents a summary of work accomplished during the period November 27, 1967, through January 31, 1968, on the study of the ultrahigh vacuum frictional-adhesional behavior of silicates as related to the lunar surface. This work is being conducted for the Office of Advanced Research and Technology, National Aeronautics and Space Administration, under contract NAS7-307.

1.2 Purpose of Program

The purposes of this program are (a) to obtain quantitative experimental data concerning the ultrahigh vacuum adhesional behavior of silicates (present at the lunar surface) in contact with other silicates and with various non-silicates (principally metals), (b) to achieve an understanding of the mechanisms responsible for the observed adhesion, and (c) to investigate techniques for reducing or eliminating the adhesion.

1.3 Approach

The approach used during this report period has been (a) to cleave silicates at ultrahigh vacuum and contact the freshly-formed surfaces with contaminated, sputtered, and mechanically abraded metal surfaces, and (b) to measure the surface distribution of electrostatic charge produced by ultrahigh vacuum cleavage of silicates. Approach (a) serves to provide information concerning the adhesional behavior of silicates in contact with metals with the various surface states which may be present during lunar missions. Approach (b) serves to provide information concerning the mechanisms which may be responsible for the observed surface charging, and hence the range of adhesional phenomena which may occur on the moon.

1.4 Item of Interest

A paper has been prepared and submitted to the Journal of Geophysical Research. This paper summarizes our results to date on the adhesional phenomena associated with ultrahigh vacuum cleaved silicates.

2.0 INSTRUMENTATION AND TECHNIQUES

Major instrumentational changes were made during this reporting period. These changes were necessary in order to study the effects of surface state of metals upon the adhesion between metals and vacuum cleaved silicates, and to investigate the causal mechanisms for the observed silicate surface electrostatic charging. These changes consisted of (a) installation of equipment to permit sputtering and mechanical abrasion of metal surfaces, and (b) fabrication of a second vacuum system with associated components for measuring charge distributions on silicates.

2.1 Silicate-Metal Adhesion as a Function of Metal Surface State

The system constructed for studying this is shown in Figure 1. The length of the silicate sample to be cleaved has been extended and multiple cleavage notches have been added. The purpose of this modification is to allow multiple cleavages to be made under a variety of metal surface states without opening the system. The silicate sample is suspended on a wire attached to the spring used to measure adhesion force (see previous reports for description of adhesion measuring device). The metal sample is press-fitted into a circular hole cut in a glass disk. The sample rests on a second glass disk. The purpose of these disks is to electrically insulate the metal sample from the vacuum system walls, which are maintained at ground potential. A high voltage, insulated, lead wire

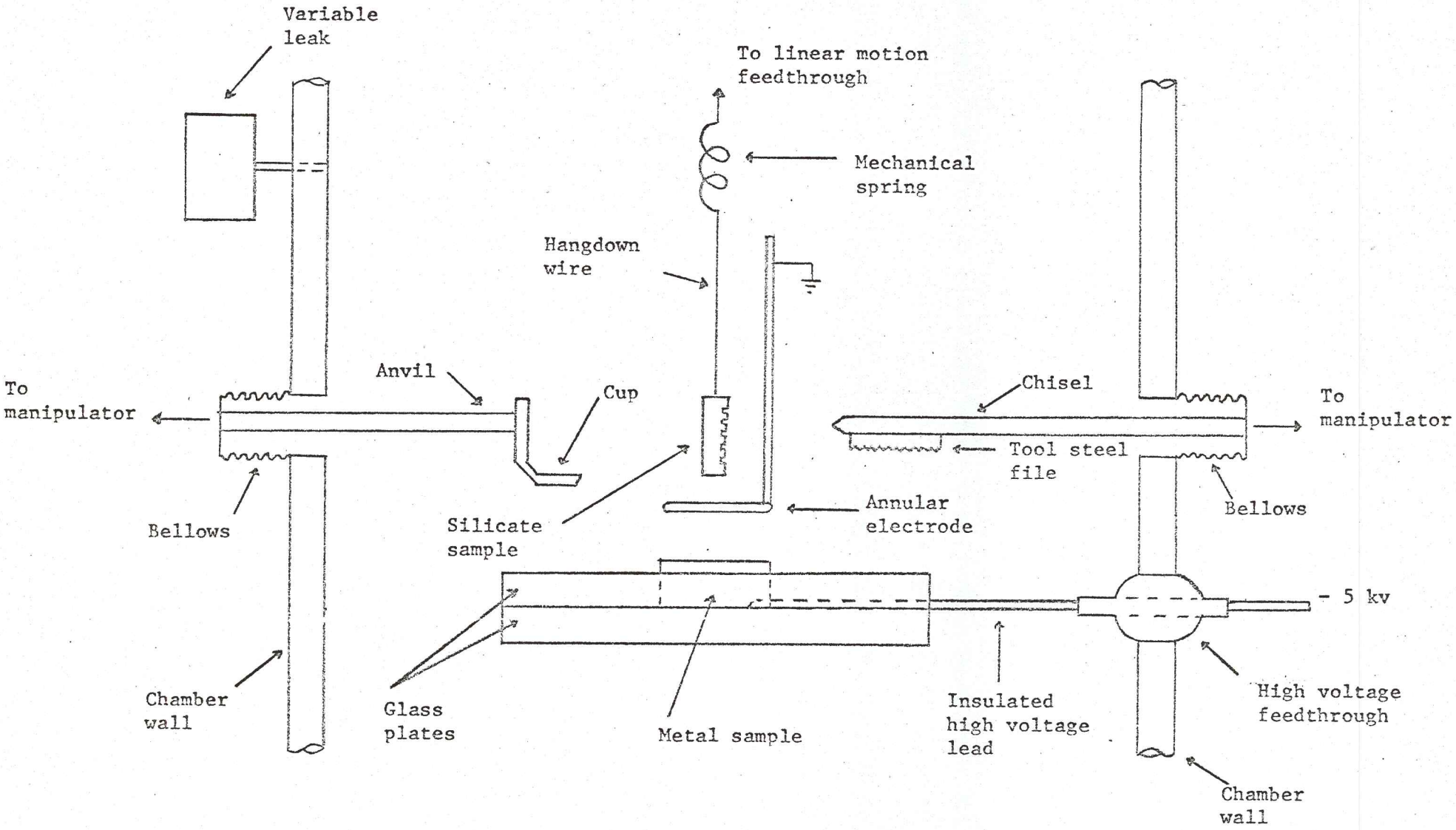

Figure 1. Schematic of experimental apparatus for the study of adhesion between vacuum cleaved silicates and metals having various surface states.

is inserted into the metal sample. This wire is also connected to a high-voltage feedthrough in the chamber wall. A second heavy wire, whose lower end is shaped into an annulus colinear with the silicate sample, is attached to the device supporting the mechanical spring. The function of these wires is to permit sputter cleaning of the metal surface. To do this, purified argon is admitted to the system to several microns pressure, then a D.C. voltage of up to -5 KV is applied to the metal sample.

The argon supply system consists of an argon tank, a purifying chamber and a variable leak. The purifying chamber contains a mixture of 50 Ti - 50 Zr (atomic percent) chips through which the argon must flow, and a heater to heat the chamber up to 800°C. Passage of the argon through the heated chamber suffices to effectively remove all CO_2, CO, N_2, O_2, H_2 and H_2O from the argon. The measured frost point of the purified argon is -84°C which corresponds to only 0.15 ppm of H_2O impurity remaining. A mass spectrometer will be mounted to the system to monitor gas impurity content.

Finally, a high carbon steel file is mounted to the base of the cleavage chisel. (Figure 1) This file is utilized to mechanically abrade the metal sample surface. A small pan is mounted to the base of the anvil. The purpose of this is to catch cleaved sections of the silicate sample so that they will not contact the metal sample surface.

The general procedure of operation of the experiment is as follows:

a. The system is evacuated to ultrahigh vacuum (10^{-10} torr).
b. The silicate sample is cleaved and the fresh silicate surface contacted with the contaminated (cleaned solely by exposure to ultrahigh vacuum

and moderate heat) metal sample surface.

c. The resultant adhesion is measured as a function of time.

d. Purified argon is then admitted to the system through a variable leak, with the ion pump off.

e. The system is flushed with argon utilizing a forepump system. Pressure is monitored with a millitorr gage.

f. The argon flow and pumping are then stopped with a system argon pressure of several microns (nominally 30-300μ).

g. Sputtering of the metal sample surface is then begun by applying high voltage (D.C.) to the electrodes.

h. Following the sputtering, the silicate sample is cleaved again and contacted with the sputter-cleaned metal sample surface. Adhesion force is measured as a function of time.

i. The metal sample is then sputtered again and the system evacuated to ultra-high vacuum.

j. The silicate sample is cleaved a third time and contacted with the sputter-cleaned metal. Adhesion force is measured as a function of time.

k. Sufficient oxygen is then admitted to the system to ensure complete oxidation of the metal surface.

l. The system is then re-evacuated to ultrahigh vacuum.

m. The metal surface is mechanically abraded using the file attached to the cleavage chisel.

n. The silicate sample is then cleaved a fourth time and contacted with the abraded metal. Adhesion is measured as a function of time.

o. The system is raised to atmospheric pressure and opened.

This is the basic experimental approach, but it should be noted that as many notches as possible are formed on each silicate sample to permit more than the minimum required number of cleavages to be made, and hence to permit

modification of the experimental procedure as desired or required.

2.2 Surface Charging

Two methods are being used to measure the electrostatic charge distribution on vacuum cleaved samples. The first method is the measurement of the integral of the current induced onto a metal probe

$$Q = \int i dt$$

using an electrometer amplifier. This measures the scaler charge density averaged over the probe surface. The second method, which is being developed, is to measure the magnitude and direction of displacement of a metallic sphere attached to the end of a wire arm, which acts as a spring support, when the potential of the sphere is varied by an external variable voltage power supply. Measurements from two orthogonal directions are needed to find the vector force since the probe presently has only two degrees of freedom.

A stainless steel ultrahigh vacuum system has been built for the surface charging experiments. It consists basically of a 15 cm I.D. manifold connected to a 500 liter/sec sputter-ion pump. A Bayard Alpert ionization gage, a millitorr vacuum gage, a UHV bakeable vacuum valve for rough cryo-pumping of the system with sorption pumps, a window, a UHV variable leak, and a mass spectrometer are connected to this manifold through sideports. The cleavage manipulator system is attached to the front face of the manifold through a reducing flange. It is comprised of two standard crosses and one specially designed cartesian cross (Figures 2 and 3). Two view ports are disposed at right angles to one another so that the sample can be viewed parallel and perpendicular to its cleavage face. The sample rotates with respect to the electrometer probe reducing noise inevitably associated with moving the probe. Charge is measured from an

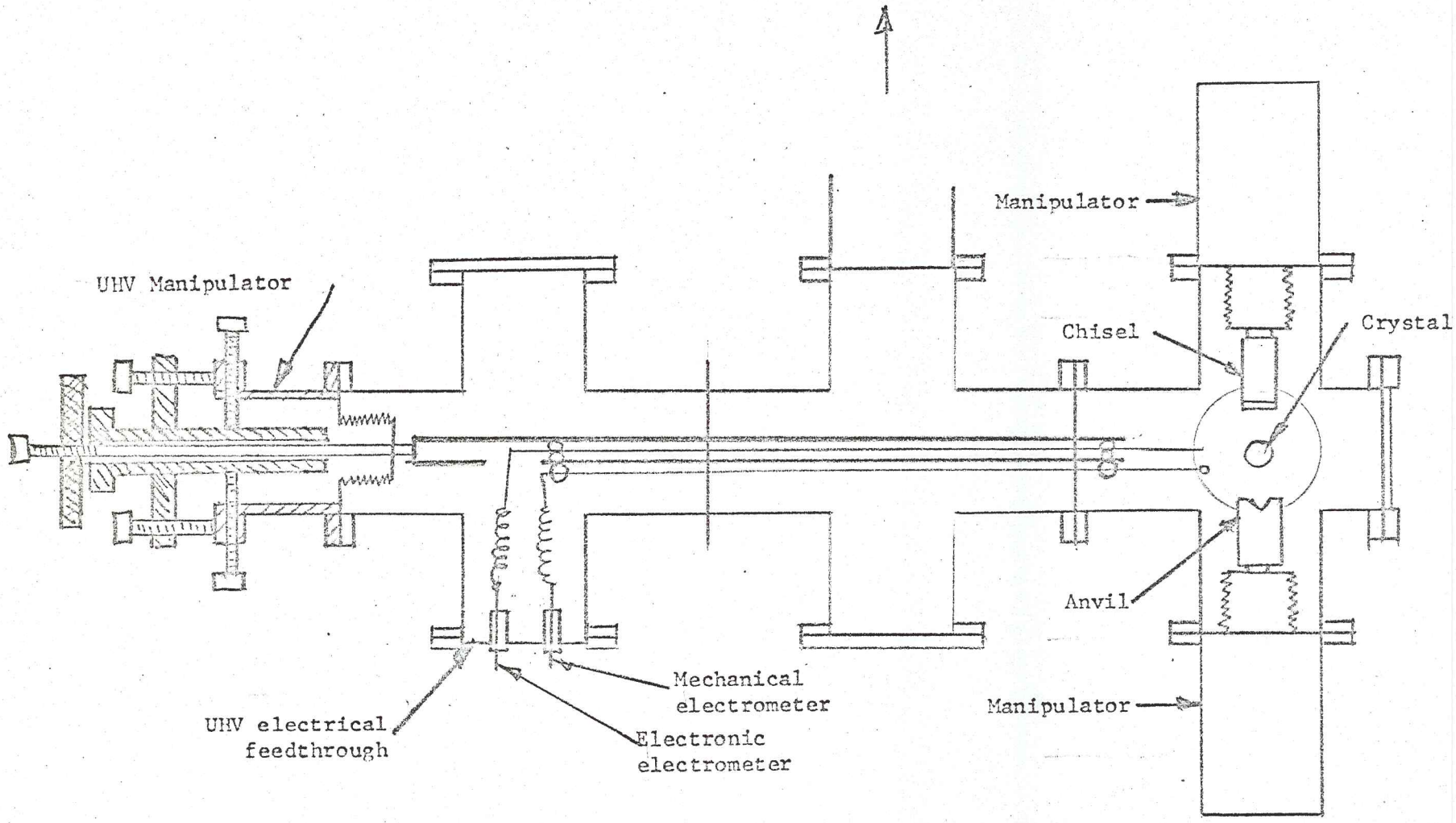

Figure 2. Experimental apparatus for measuring surface charge.

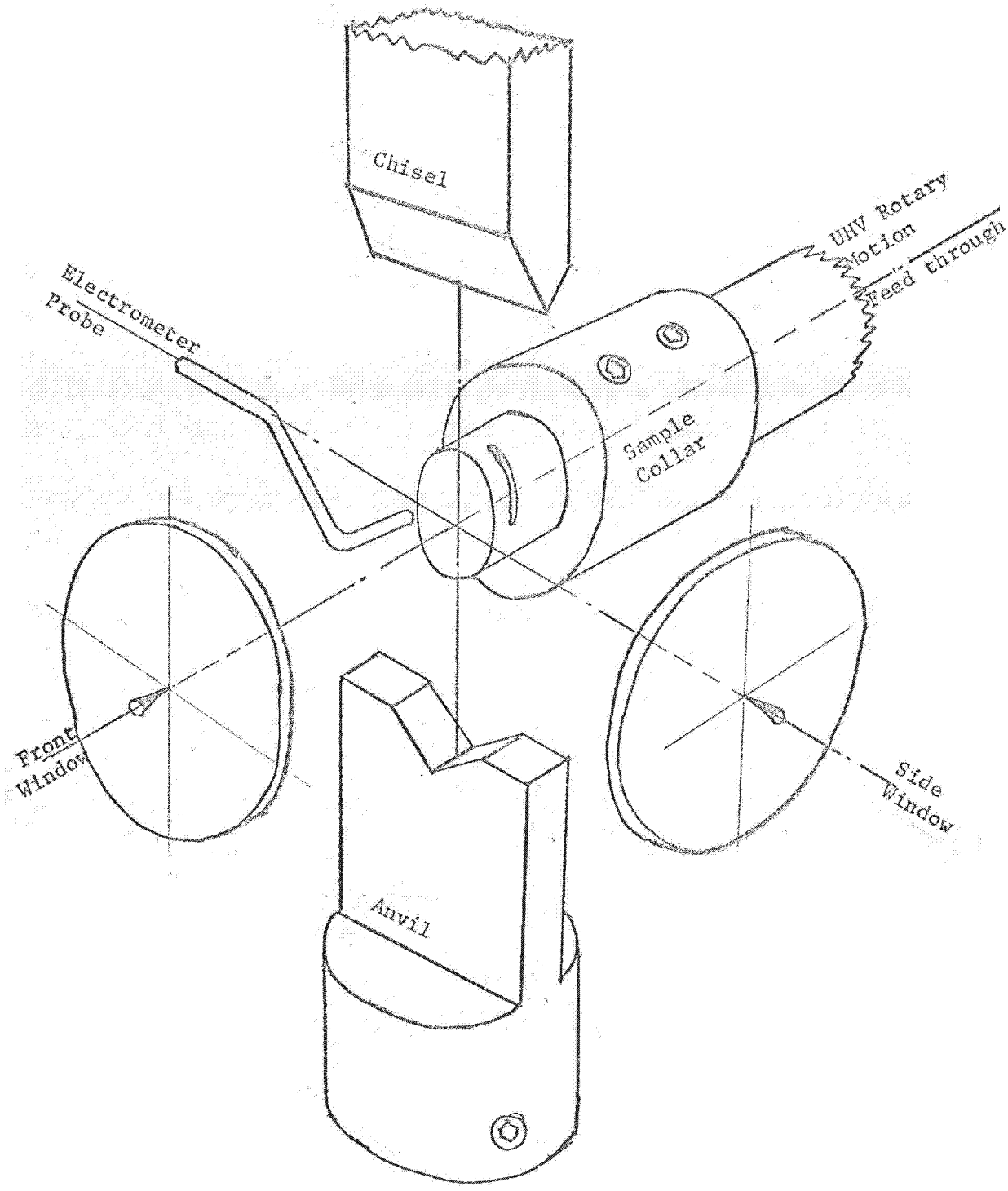

Figure 3. Cartesian cross configuration for cleavage and charge measuremen

arbitrary reference point which can be made the system ground-potential.

The cleavage chisel and anvil are at right angles to the electrometer-crystal-window plane, and can be moved into position for cleavage and then withdrawn for measurements. A schematic of one of the three identical manipulators is shown in Figure 2. This manipulator is for the electrometer probe. The other two are for the chisel and anvil. These manipulators are similar in design to those described in previous quarterly reports.

The electrometer probe UHV vacuum feedthrough has a resistance to ground in excess of 10^{15} ohms. A Keithley 610B electrometer is connected directly to the feedthrough to reduce system noise. The electrometer is operated as a coulometer, using capacitive feedback. The grid current of the input tube makes it necessary to apply a drift correction which is approximately 5% (maximum) at the highest sensitivities used to date.

Experimental operation is as follows. After UHV is attained the rotary motion feedthrough upon which the sample is mounted is locked in place. A binocular microscope is used to assist in positioning the anvil under the crystal and the chisel into a notch in the sample. Pressure is then applied to the sample by means of modified C clamps attached to the anvil and chisel manipulators. Cleavage is then obtained by rotating the chisel control knob slightly which increases the pressure to the required amount. Cleavage occurs by the side faces of the chisel wedging the sample apart. After cleavage, the anvil and chisel are withdrawn and the electrometer probe moved into position. The sample is rotated and the angular position measured by the voltage output of a

belt driven potentiometer. The sample charge and angular position are recorded with a Leeds and Northrup two channel recorder. Since the electrometer probe itself is moveable, the charge distribution over the entire surface is obtained. A sample trace of charge distribution as a function of sample orientation is shown in Figure 4.

3.0 EXPERIMENTAL DATA

3.1 Vacuum Cleaved Silicate-Metal Adhesion

As of this writing the first run has just begun. The silicate sample is microcline which is cleaved along the (001) plane. The metal sample is aluminum alloy (2024). Three cleavages of the microcline have been made at a pressure of 3×10^{-10} torr. A pressure burst to $\approx$ 1-2 $\times 10^{-8}$ torr was observed during the first cleavage, to 2×10^{-8} torr during the second, and to 3×10^{-8} torr during the third. Contact was made with the contaminated aluminum. No definite indications of adhesion were detected.

3.2 Surface Charging

Two runs have been made to date, the second run not as yet being completed.

Run #1: A 5 mm diameter orthoclase crystal was cleaved at 1.5×10^{-10} torr in the b-axis direction on the (001) basal plane. The electrometer probe, 0.5 mm from the side of the crystal, registered a positive charge relative to its precleavage state. After a 15 second interval the charge increased spontaneously by a factor of ten to about 2×10^{-11} coulombs ($\sim 10^{8}$ charges). As the anvil and chisel were moved away from the cyrstal the measured charge fluctuated and 2.3 minutes after cleavage the electrometer went off scale positive, saturated the input, and the reference zero was lost when a new capacitor was inserted in switching from the 10^{-10} scale to 10^{-9} scale.

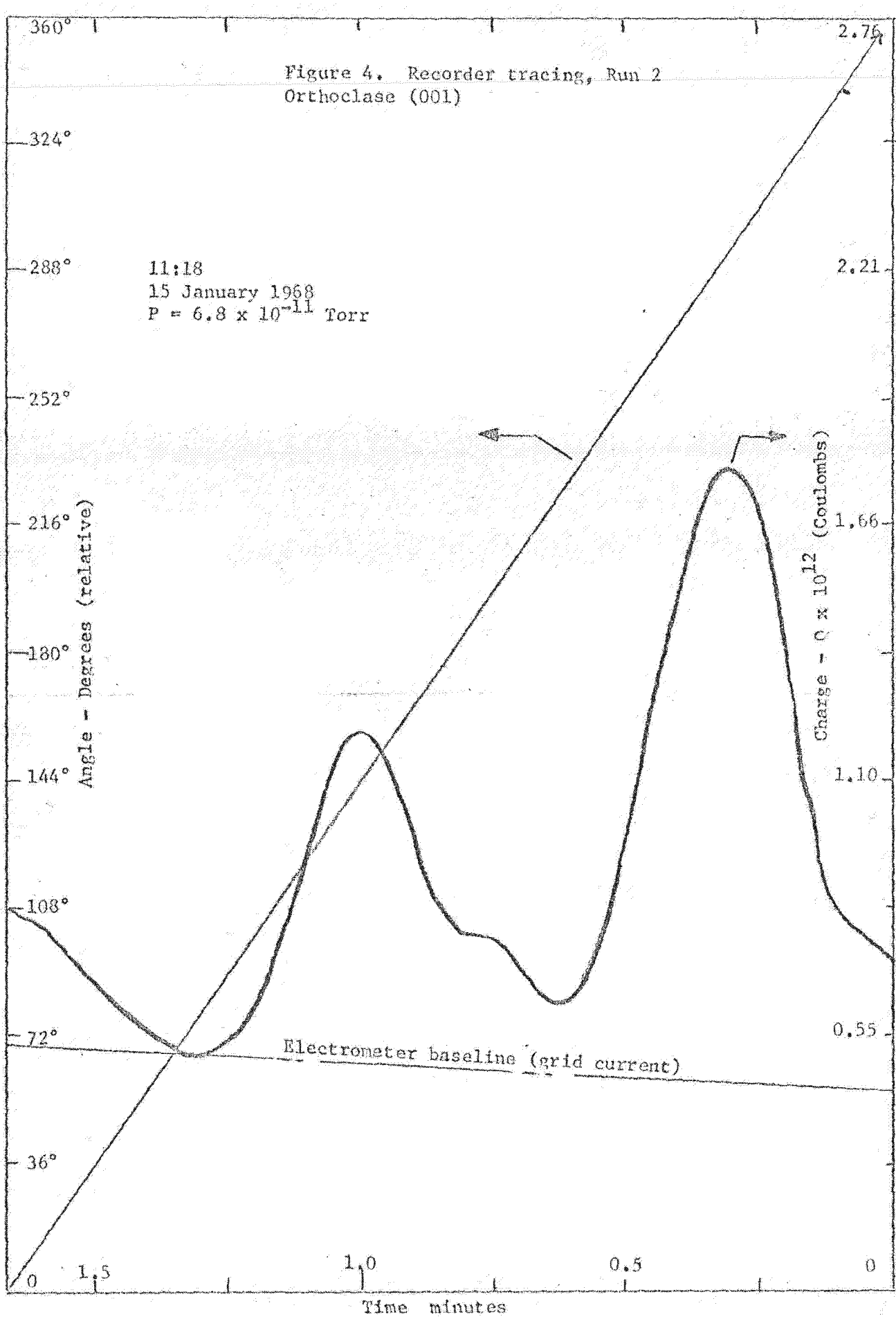

Figure 4. Recorder tracing, Run 2
Orthoclase (001)

Measurement of the charge distribution by rotating the crystal while keeping the electrometer probe fixed showed that the relative charge distribution was quadrupolar in shape. The more negatively charged regions showed alignment with the b-axis and the more positively charged regions were aligned with the a-axis, Figure 5. This orientation persisted throughout the experiment, although repositioning the probe changed the magnitude of the more positive peak with respect to the less positive valley.

An attempt was made to establish a new zero relative to ground by moving the anvil between the electrometer probe tip and the orthoclase crystal face, and grounding the electrometer probe tip to the backside of the anvil. This procedure was only partially successful because the probe was not shielded completely from the electric field surrounding the charged crystal. Although there is no doubt about the positively charged regions being positively charged with respect to ground, the experimental results are inconclusive about assigning a negative or positive sign to the least positively charged region.

Between 30 and 70 hours after cleavage, the electrometer probe position was held fixed and periodic measurements made of the relative change in the maximum charge difference. Within experimental error the charge remained constant during this 40 hour period. It corresponded to a measured difference in charge of 8×10^9 charges when the tip of the probe was .2 mm from the surface and 1.5 mm from the center of rotation.

A test of the mechanical electrometer probe showed it to be too sensitive when the lever arm was nearly 1 cm. The sphere was attracted to the more negatively charged region and touched the surface without affecting the total charge. A

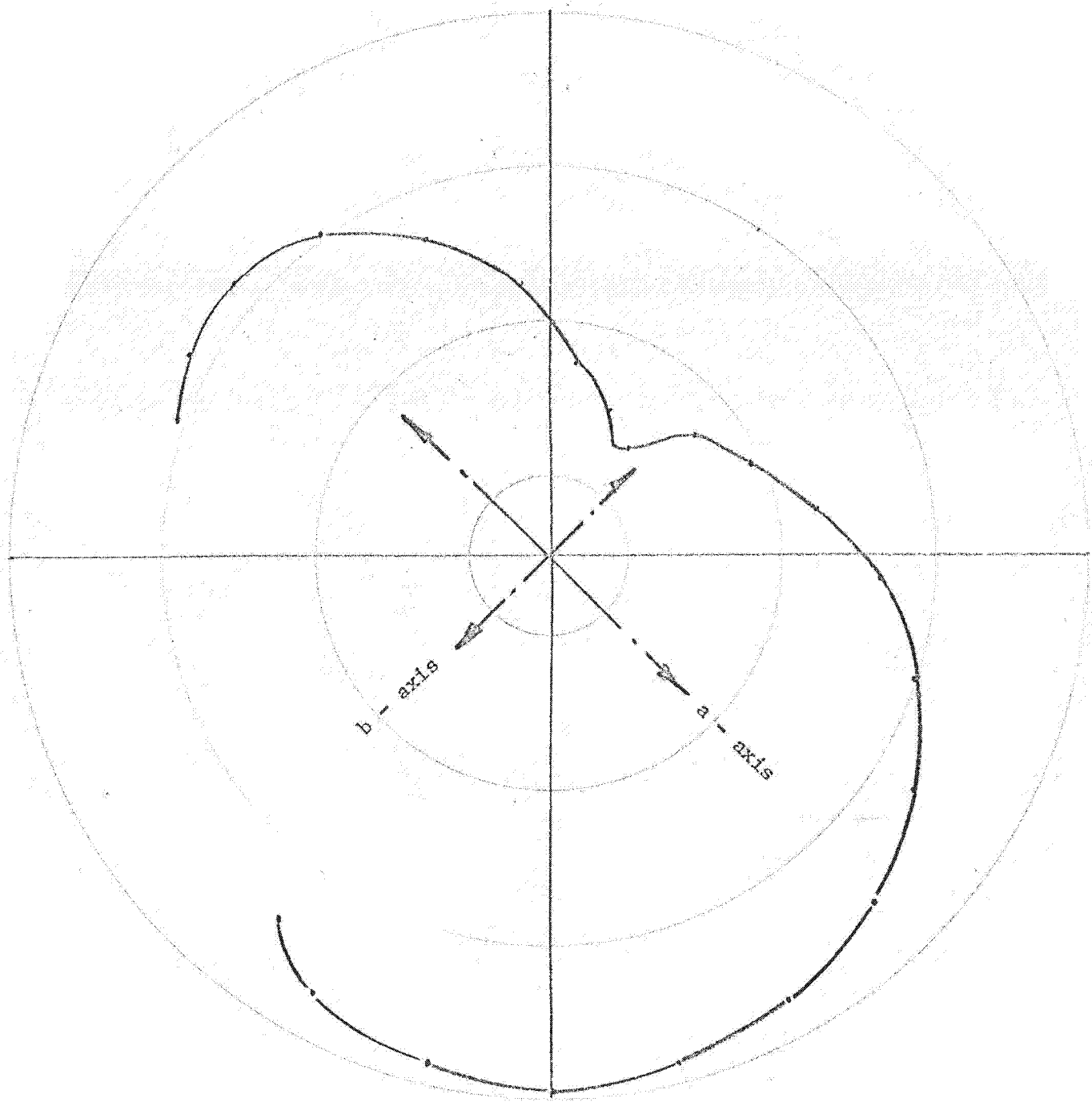

Figure 5. Polar plot of charge distribution Run 1, 50 minutes after cleavage.

positive bias on the probe deflected the spherical probe parallel to the surface and away from the crystal center with respect to a positively charged region when oriented as shown in Figure 6a. When near the negative region, Figure 6b, the probe was attracted towards the crystal, both in the plane as shown and perpendicularly to the plane.

Mass spectra of the background gas in the system at 3×10^{-10} showed the main components to be H_2O, CO, and CO_2. N_2 and a variety of hydrocarbons were also found, the hydrocarbons originating in the spectrometer which had not been baked out well.

Seven days after cleavage, the system was backfilled with a dry nitrogen-argon mixture (nominally dry nitrogen). The pressure was increased to 8×10^{-5} torr and the ion pump turned off. Pressure was monitored to 1 torr with the millitorr vacuum gage and recorded simultaneously with the electrometer output of the peak to peak variation of charge as the sample was rotated. The rate of pressure rise was controlled by a bakeable UHV variable leak valve and the rate was held to approximately one decade of pressure in 2-1/2 minutes.

Figure 7 shows a plot of the peak to valley charge amplitude as a function of pressure. No change in the amplitude was observed from 10^{-10} torr to 10^{-3} torr and hence this pressure region is not shown. The charge was observed to decrease pulse-wise at .014 torr, .033 torr and .088 torr. The curvature is real and may be associated with time rather than pressure.

Run #2: The second orthoclase sample was notched for cleavage in three directions, along the a-axis, b-axis, and intermediate to the two, to test the relationship between the charge distribution, the cleavage direction and the crystal axes.

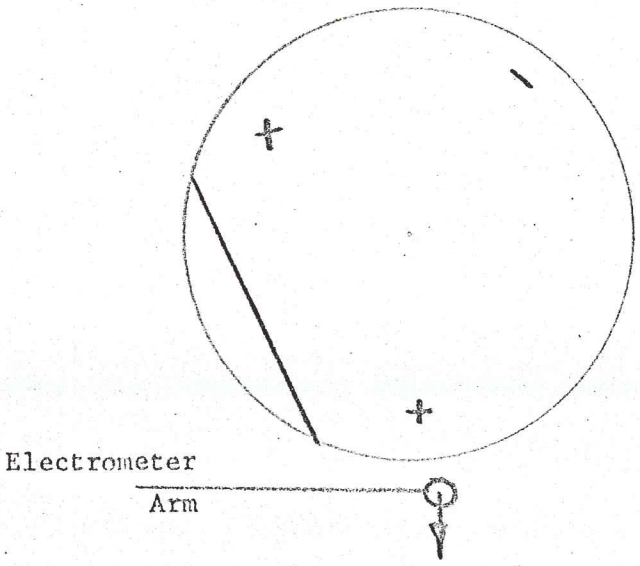

Figure 6.a

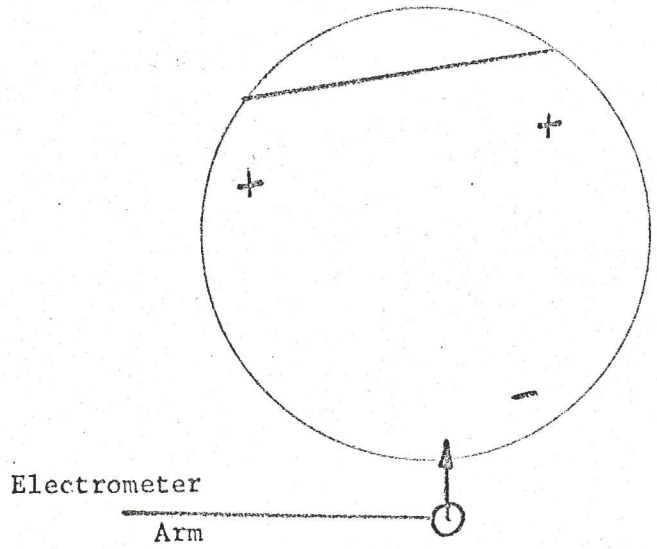

Figure 6.b

Figure 6. Mechanical electrometer probe displacement when probe biased positively relative to ground. Run 1

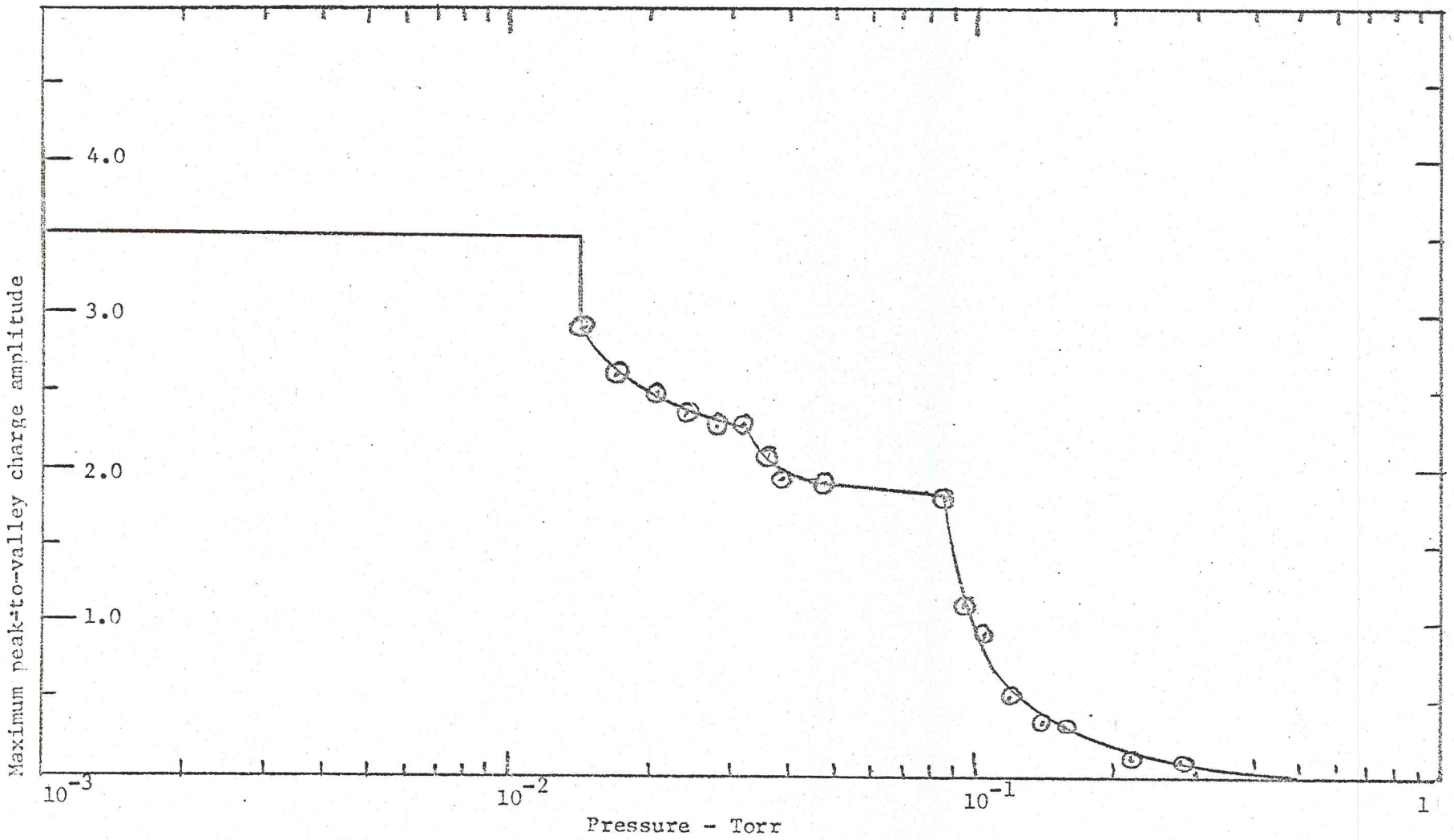

Figure 7. Variation in charge density as the system pressure was raised with a dry nitrogen-argon mixture, Run No. 1.

Prior to mounting the sample in vacuum, a trial run in air demonstrated that the crystal could be cleaved successfully in these directions.

In this second run that started with cleavage in the intermediate direction at a pressure of 3×10^{-10} torr, it was decided that the probe should be moved into position as rapidly as possible and kept fixed for the entire run so that the time history of the charge could be measured without ambiguity. The electrometer registered a positive displacement upon cleavage even though the cleaved section of the crystal was held securely to the base section by the electrostatic attraction. After a few unsuccessful attempts to wedge the crystal slab away with the chisel, the anvil was moved under the cleaved slab with the chisel held in the pre-cleavage notch. Movement of the anvil and chisel moved the cleaved slab upward and out onto the anvil notch. As the anvil was lowered and the top of the slab crystal came into line with the center of the base crystal, the slab flipped forward and adhered to the front face of the anvil along its edge. Some time later, the crystal lay down on its face as shown in the Figures 8 and 9. During the course of the experiment (one month) the crystal slab has slowly moved down the face of the anvil until it came to rest at the base. The cleaved face of this sample lies against the anvil as seen in the photographs.

It took 10 minutes to dislodge the crystal slab and withdraw the chisel and anvil. The sample was rotated with the electrometer probe 5 mm from the crystal surface and a dipolar charge distribution was observed with a 150° angle between the maximum and minimum. A shoulder was observed which later split into two arms of a quadrupolar charge distribution as the probe was moved into position over the face of the crystals. This movement was completed 13 minutes after cleavage and the electrometer probe remained fixed for the rest of the experiment. A rotation trace

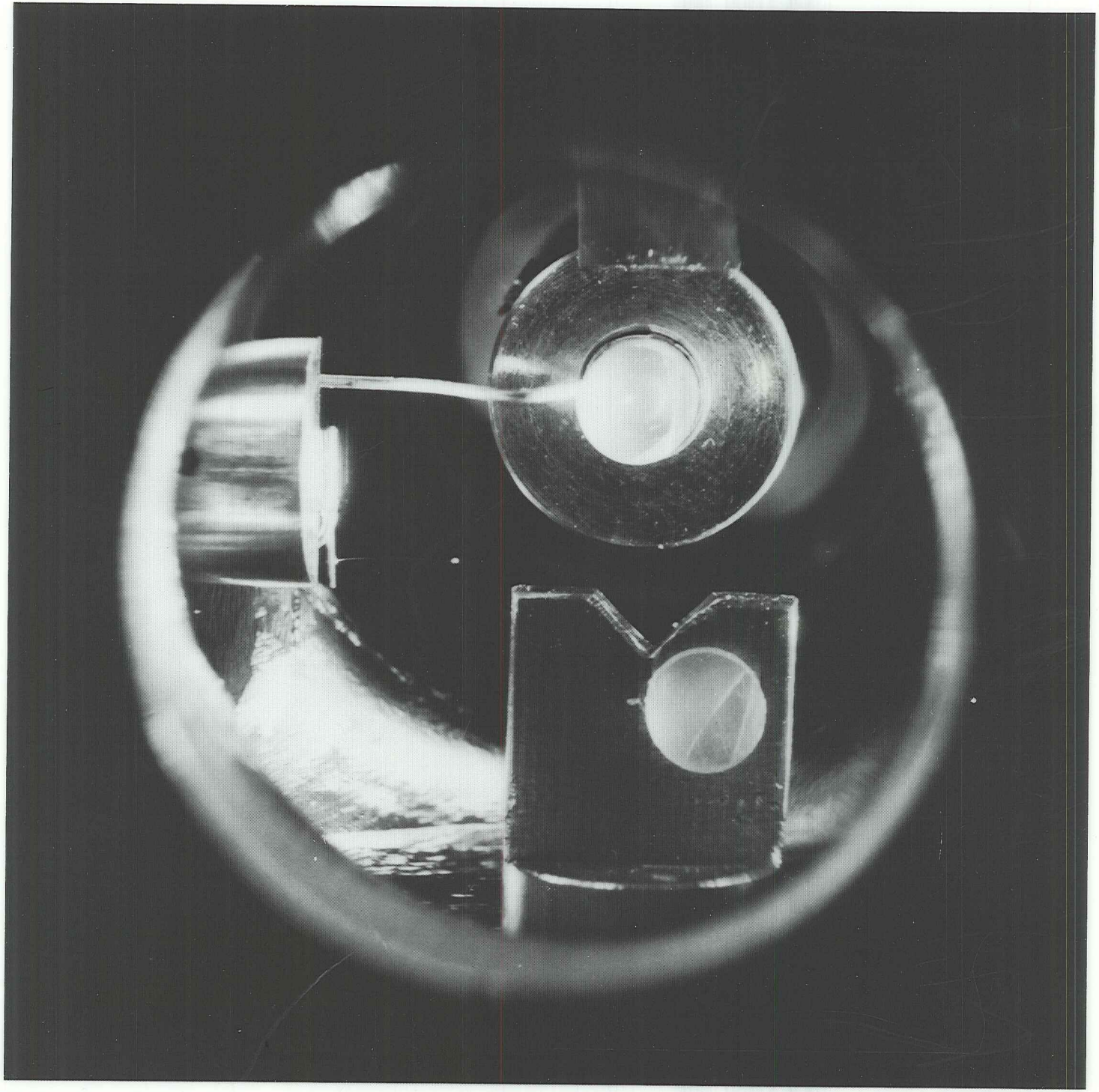

Figure 8. Front view - Orthoclase cleavage on (001) plane, 4x magnification, run 2.

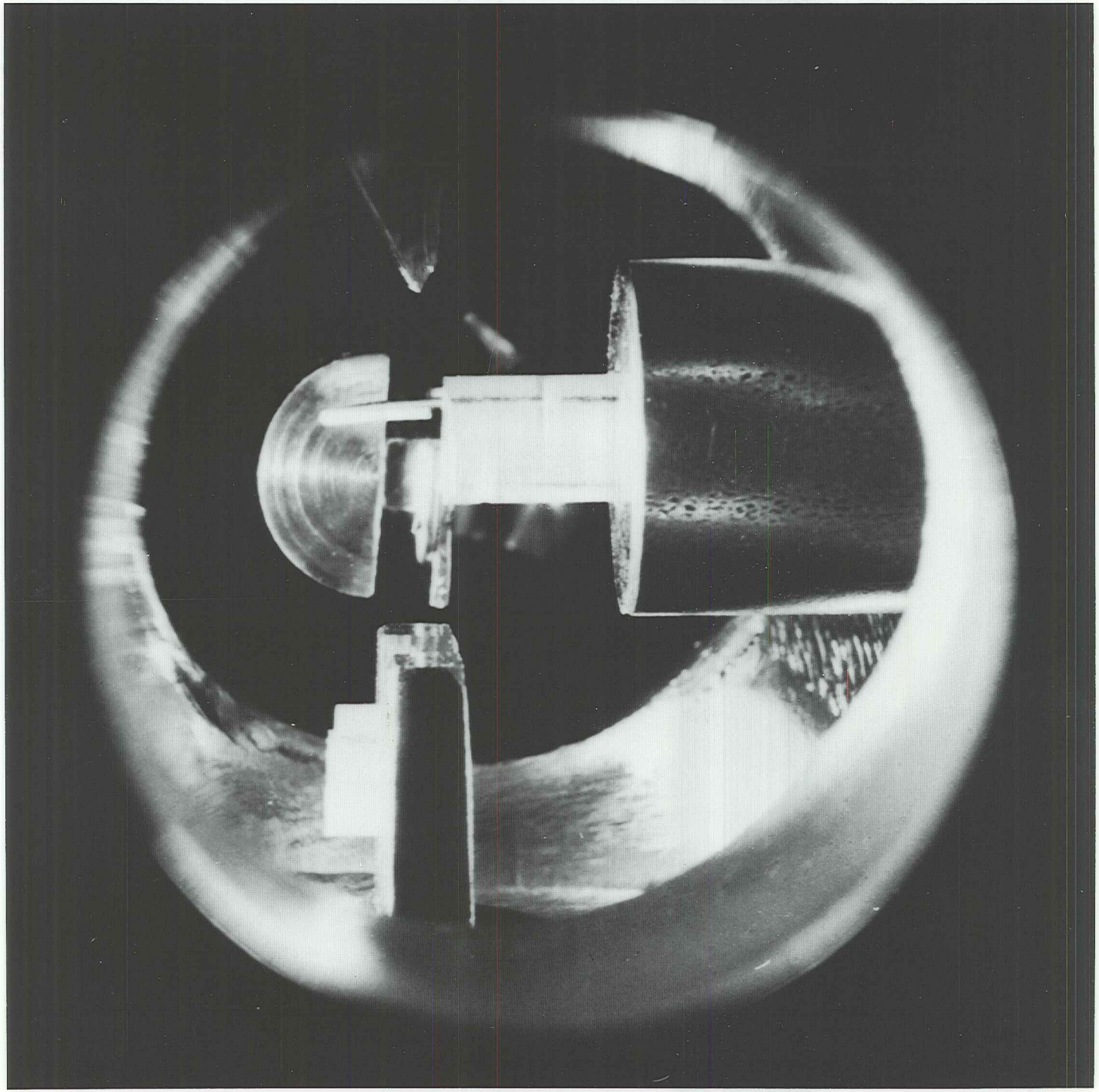

Figure 9. Side view - Orthoclase cleavage on (001) plane, 4x magnification, run 2.

is shown in Figure 4.

Tracings of the charge distribution during the first three hours are shown in Figure 10. The time history of the maximum peak to valley amplitude is given in Figure 11. Superimposed on this plot is the time variation in adhesion measured by J. A. Ryan and reported in previous quarterly reports.

On the ninth day after cleavage, a UV mercury light source was used to irradiate the sample through the pyrex glass window (nominal cutoff at 3000Å). The peak to valley charge ratio decreased to 2/3 its value after 24 hours, continued to decline another 10% after the UV source was turned off and then recovered the next day. The cause of this variation is obscured by a cyclic drift in peak values through the day. A He-Ne laser (6328Å) beam used for 42 hours produced an apparent decrease in charge magnitude. However, the amount of decrease was not sufficiently large to conclude that it was definitely associated with the irradiation.

The quadrupole distribution is oriented generally along the crystallographic axes. The exact orientation will be determined after the crystal is removed from the vacuum system.

4.0 DISCUSSION

4.1 Vacuum Cleaved Silicate-Metal Adhesion

Nothing much can be said as yet about this adhesion since the first experimental run has just begun. The three cleavages of microcline performed to date did not produce detectable adhesion between the fresh silicate and contaminated metal surfaces. Significant gas bursts occurred during each cleavage and these could

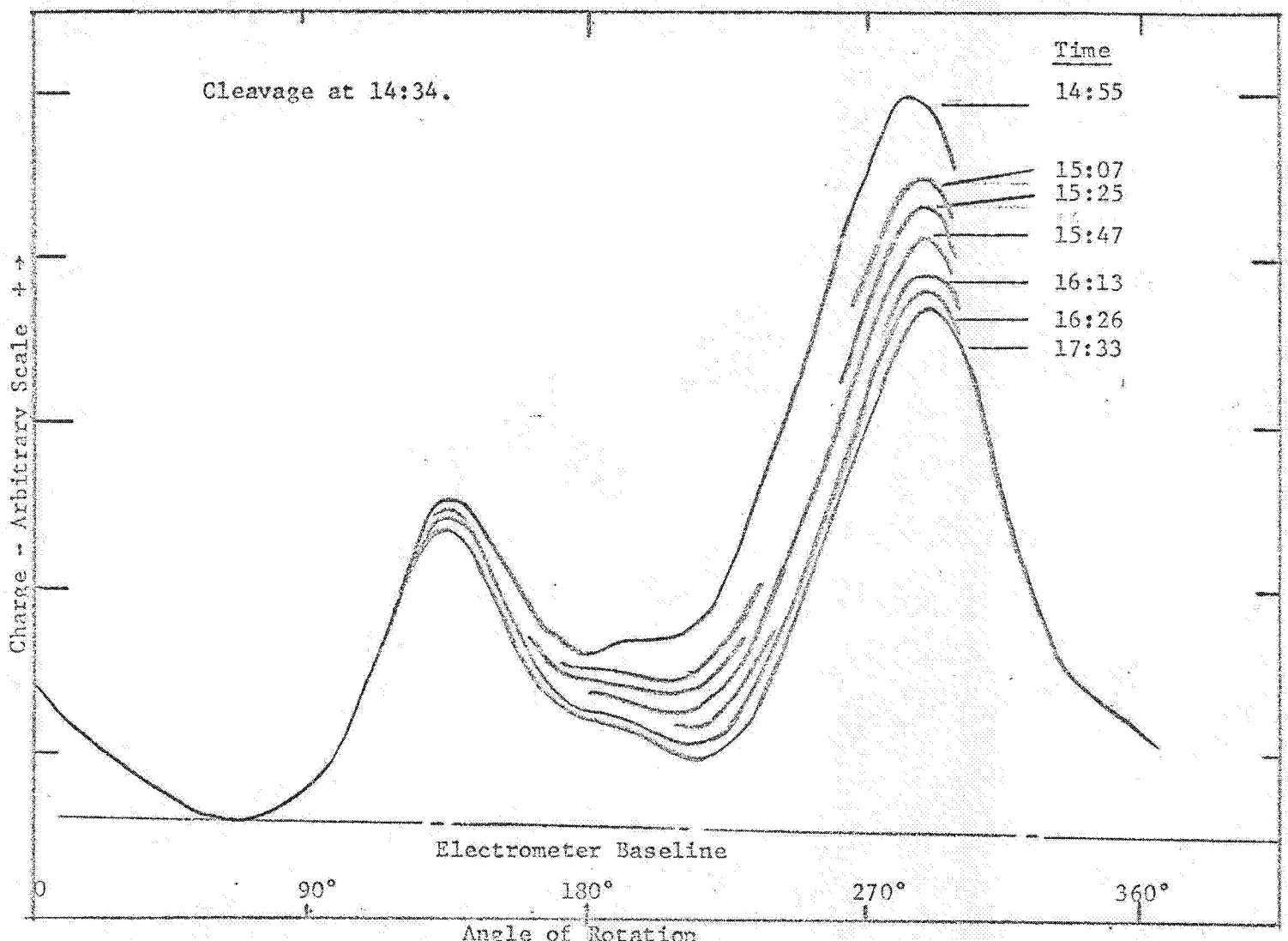

Figure 10. Variation in magnitude and shape of electrostatic charge distribution after cleavage.

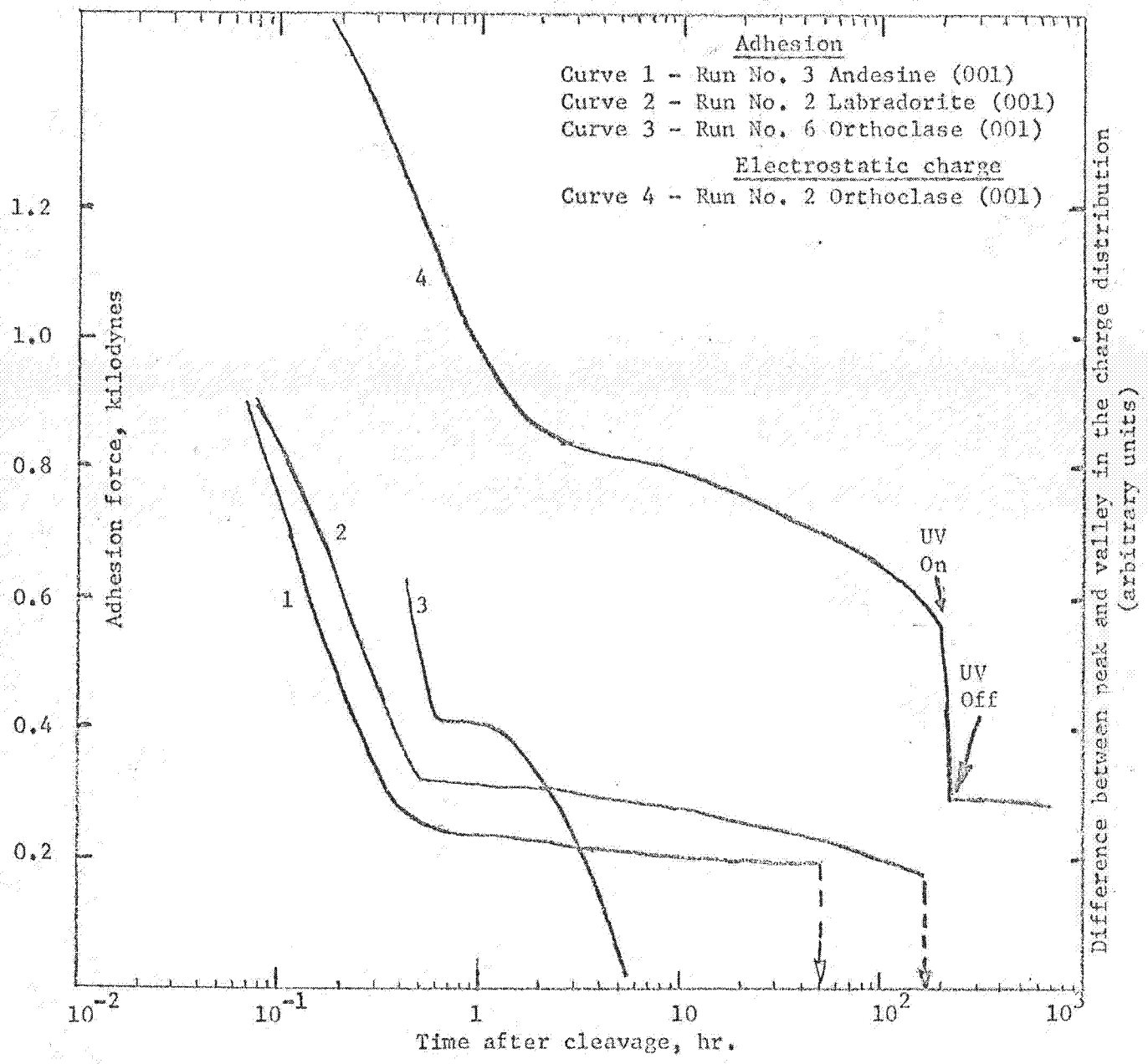

Figure 11. Comparison of the time variation in the adhesion force and the electrostatic charge after UHV cleavage.

be responsible for destroying the adhesion (the effect of gas bursts in reducing adhesion has been discussed in previous reports). It is of interest to note that in the surface charging experiments (discussed in the following section) where essentially no gas bursts occurred, the fresh silicate surfaces did adhere, and relatively strongly, to contaminated metals.

4.2 Surface Charging

The angular relationship between the quadrupolar charge distributions and the crystallographic axes in the first two runs suggests that a dominant mechanism in the steady state charge distribution is related to non-uniform polarization of, and conduction in, an anisotropic dielectric. Externally, the charge appears to be dipolar but on the face it is quadrupolar. A firm interpretation of this experimental result is premature because the unshielded probe is not measuring a local charge density but an average value since it was designed for maximum sensitivity (the results show that such sensitivity is not required so it is being re-designed, incorporating a guard electrode).

Electrical conductivity is playing an important role as seen both in the magnitude and in the change of shape of the distribution, Figure 10. This happens mainly during the first hours after which the decay is very much slower. The sharp break in the curve at the end of an hour suggests that two or more phenomena are involved. Although surface conductivity is normally considered a fast process, the background gas may be contributing significantly to the observed discharge. At 3×10^{-10} torr it takes approximately one hour to have a monolayer of gas strike the surface. This correlation strongly suggests that surface reaction with high energy sites is producing ions which can migrate and neutralize charge sites. When the surface reactive sites are filled, the surface is

"passivated" and the remaining charge is stabilized.

Ultraviolet light can cause the observed decrease in charge by one of three processes:

(a) photoelectric emission from the crystal surface;

(b) photoelectric emission from the chamber walls;

(c) photoconductivity in the crystal.

Further experimental work is required to clarify the mechanisms. This is an important problem with respect to the stability of electrostatic charges on the lunar surface or in space since photoelectric emission can act as a charge stabilizing force whereas photoconductivity will dissipate the charge. The stability of the charge for over 20 days in vacuum demonstrates the slowness of the spontaneous discharge process.

Stability of the charge up to 10^{-2} torr shows that in relation to the initial surface interactions, the surface is passivated. The discharge pulses at pressures ranging from 10 to 100 microns suggest strongly that gaseous breakdown is responsible for the discharge process. Sample calculations give estimates of the fields to be 10^{6} volts/meter and in the same pressure range self-quenching plasma breakdown sparks should recur as the pressure increases, until a sustained breakdown reduces the charge below the sensitivity of the electrometer. Consequently this is a complicated, geometry dependent process.

The mechanical electrometer was found to operate and as predicted shows promise for measuring the electrostatic vector field. Future use of this device is planned.

Two additional points are worth note. First, during the second run the cleaved crystal section adhered to the anvil. This gives direct evidence that vacuum-formed silicate surfaces will adhere to contaminated (oxidized) metal surfaces. Indications of this had been obtained previously in several of the adhesion runs reported in prior quarterly reports. Second, Figure 11 shows an apparent striking correlation between adhesion force and charge magnitude. This indicates that the observed adhesion, even that present shortly after cleavage, is due primarily if not entirely to surface charging. It would hence be of interest to apply load force to vacuum cleaved silicates to see what effect this has on adhesion magnitude.

The second experiment will be terminated using the same dry nitrogen-argon mixture as in the first experiment. Based on this previous experience, the pressure will be raised rapidly to 10^{-3} and then very slowly to observe the time rate of discharge.

Cleavages along the a- and b-axes will be made to complete the orientation dependence measurements. After charge stabilization, the mechanical electrometer will be tested. A search for cyclic instrumental variations in the charge density will be continued and UV and laser irradiation repeated. Methods for suppressing photoemission will be tried so that photoconductivity can be evaluated separately.

The electrometer probe is being redesigned to provide a guard plane and a well defined probe area. Absolute charge density measurements can then be made. For the same reason, new shielded configurations for the mechanical probe are being considered.

On completing the next two orthoclase cleavages, different materials will be chosen from among the minerals used in the adhesion experiments. The effect of varying the post cleavage background pressure and composition is also of interest for studying the activity of the freshly cleaved surface, and the effectiveness of various gases in reducing the charging.

5.0 SUMMARY

Primary effort during this quarter has been applied to modifying the vacuum chamber utilized in previous experiments and constructing a second vacuum system to study the surface charging. The original system now possesses the capability for argon ion sputtering and mechanical abrasion of metal surfaces. The first run has begun with this system but no data are as yet available.

Two runs have been made with the second system, the second of which has not as yet been completed. Charge magnitude and distribution over the (001) surface of ultrahigh vacuum cleaved orthoclase has been measured. Relatively large charge magnitudes have been indicated. The charge distribution appears to be quadrupolar with an orientation associated with the crystal axes and possibly with the direction of cleavage. After the first hour or so following cleavage the charge becomes stable with little subsequent decrease (the longest run to date was for 30 days at which time the charge was still present and significant).